

# Improved Quantum Theory of Many-Electron Systems. IV. Properties of GF Wavefunctions\*

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The GF method for obtaining accurate many-electron wavefunctions was described in a previous paper. In this paper, some of the properties of this method are explored, and it is shown that the Hellmann-Feynman, Koopmans', and Brillouin's theorems apply to GF wavefunctions. Calculations are reported on  $\text{Li}_2$ ,  $\text{CH}_4$ , and  $\text{CH}_3$  in order to demonstrate some aspects of the method.

## I. INTRODUCTION

In the preceding paper<sup>1</sup> (called III) we derived the GF method of obtaining accurate many-electron wavefunctions. This method is more accurate than, and removes several defects of, the Hartree-Fock method but at the same time still allows an independent particle interpretation of the many-electron wavefunction. In this paper we will continue the development by investigating some properties of the GF wavefunctions.

We take our Hamiltonian as

$$H(1, 2, \dots, N) = \sum_i -\frac{1}{2}\nabla_i^2 + \sum_i V(i) + \sum_{i>j} (r_{ij})^{-1} \\ = \sum_i h(i) + \sum_{i>j} g(i, j), \quad (1)$$

where  $V(i)$  is the potential due to the nuclei,  $h(i) = -\frac{1}{2}\nabla_i^2 + V(i)$  is a one-electron operator, and  $g(i, j) = (r_{ij})^{-1}$  is a two-electron operator. The GF method consists of finding the best approximation to an eigenstate of (1) by a wavefunction of the form

$$G_f^\gamma(\Phi\chi), \quad (2)$$

where

$$\Phi = \phi_{1a}(1)\phi_{2a}(2)\cdots\phi_{na}(n)\phi_{1b}(n+1)\cdots\phi_{mb}(N), \quad (3)$$

$$\chi = \alpha(1)\alpha(2)\cdots\alpha(n)\beta(n+1)\cdots\beta(N), \quad (4)$$

and  $G_f^\gamma$  is an operator defined in I<sup>2</sup> involving permutations of the spatial and spin coordinates of the  $N$  electrons. The total spin is given by  $S = \frac{1}{2}(n-m)$ ,  $\gamma = [2^m, 1^{n-m}]$ , and (4) assumes  $M_s = S$ . By requiring that the total energy be stationary under variations of the orbitals we obtained the following equations<sup>1,3</sup>:

$$H^{ka}\phi_{ka} = \epsilon_{kk}^a\phi_{ka}, \quad k=1, \dots, n \\ H^{kb}\phi_{kb} = \epsilon_{kk}^b\phi_{kb}, \quad k=1, \dots, n \quad (5)$$

where  $H^{ka}$  and  $H^{kb}$  are defined in III. The solutions of (5) are then the optimum orbitals for (3). Equation (5)

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<sup>1</sup> W. A. Goddard III, J. Chem. Phys. **48**, 450 (1968); hereinafter called III.

<sup>2</sup> W. A. Goddard III, Phys. Rev. **157**, 73 (1967), hereinafter called I.

<sup>3</sup> W. A. Goddard III, Phys. Rev. **157**, 81 (1967), hereinafter called II.

can also be expressed as<sup>4</sup>

$$\langle \delta_k \Phi | (H-E) \Theta O_{ff} | \Phi \rangle = \epsilon_{kk} \langle \delta \phi_k | \phi_k \rangle, \quad (6)$$

where from the variational conditions this must be satisfied for all  $\delta\phi_k$ .

The coupled integro-differential Eqs. (5) are solved by expanding each orbital in terms of a set of basis functions,  $\{X_\mu\}$ ,

$$\phi_k = \sum_\mu X_\mu C_{\mu k}, \quad (7)$$

thus converting (5) into<sup>5</sup>

$$H_{\mu\nu}^a C_{\nu k}^a = S_{\mu\nu} C_{\nu k}^a \epsilon_{kk}^a, \quad (8a)$$

$$H_{\mu\nu}^b C_{\nu k}^b = S_{\mu\nu} C_{\nu k}^b \epsilon_{kk}^b, \quad (8b)$$

where  $H_{\mu\nu}^a$  and  $H_{\mu\nu}^b$  are defined in III. Equation (8) and methods of solution are discussed in III. Here we examine some of the properties of the solutions and illustrate these with some calculations on  $\text{Li}_2$ ,  $\text{CH}_4$ , and  $\text{CH}_3$ .

## II. THE GF ORBITALS

### A. The Independent Particle Interpretation

From Paper II the Hartree-Fock equations are

$$\hat{H}_i^{\text{HF}} \phi_i^{\text{HF}} = \epsilon_i^{\text{HF}} \phi_i^{\text{HF}}, \quad (9)$$

where  $\hat{H}^{\text{HF}} = \hat{h} + \hat{V}_i^{\text{HF}}$ , and for the case of a singlet state with all orbitals doubly occupied,

$$V_i^{\text{HF}}(1) = \sum_{j=1, j \neq i}^{N/2} (2\hat{J}_j - \hat{K}_j) + \hat{J}_i$$

is the usual expression in terms of Coulomb and exchange operators, where

$$\hat{J}_j(1) = \int dx_2 \phi_j^*(2) (r_{12})^{-1} \phi_j(2)$$

and

$$\hat{K}_j(1) = \int dx_2 \phi_j^*(2) (r_{12})^{-1} \hat{P}_{12} \phi_j(2).$$

(Recall that the exact form of  $\hat{V}_i^{\text{HF}}$ , in particular the presence of the exchange term, is derived by applying

<sup>4</sup> The  $\delta_k \Phi$  is  $\Phi_k \delta \phi_k$  where  $\Phi_k$  is  $\Phi$  with  $\phi_k$  deleted.

<sup>5</sup> We use the Einstein summation convention for Greek subscripts, and  $S_{\mu\nu}$  is the overlap between  $X_\mu$  and  $X_\nu$ .

the variational requirement on the total energy for a Slater determinant wavefunction.) Similarly, the operator in (5) can be written as

$$\hat{H}^{ka} = \hat{h} D_{ka}^{ka} + \hat{V}_{ka}^{\text{GF}} D_{ka}^{ka}, \quad (10)$$

where  $\hat{V}_{ka}^{\text{GF}}$  contains all of the many-particle terms. Thus, if

$$\epsilon_{kk}^a \equiv D_{ka}^{ka} e_k^a \quad (11)$$

(note from Appendix B of III that  $D_{ka}^{ka} \geq 1$ ), (5) can be rewritten as

$$\begin{aligned} (\hat{h} + \hat{V}_{ka}^{\text{GF}}) \phi_{ka} &= e_k^a \phi_{ka}, \\ (\hat{h} + \hat{V}_{kb}^{\text{GF}}) \phi_{kb} &= e_k^b \phi_{kb}. \end{aligned} \quad (12)$$

Therefore, in both the Hartree-Fock and the GF methods we can interpret each  $\phi_i$  as the state of an electron moving in the field due to the nuclei (and any other nonelectronic field included in  $\hat{h}$ ) and in the average field,  $\hat{V}_i$ , due to the other electrons. This result, that the states  $\phi_i$  may be given an independent particle interpretation, is actually very important. It means that rather than examine the complicated many-electron wavefunction over the abstract  $3N$ -dimensional configuration space, we can examine one-at-a-time the simple one-particle functions,  $\phi_i$ , over the concrete easy-to-visualize 3-dimensional space. As was discussed in II, it is not true in general that a many-electron wavefunction can be given such an interpretation, not even if the many-electron wave is expressed as linear combinations of one-electron functions and not even if there are no more than  $N$  of these orbitals. In fact, in order to make such an interpretation we need to have equations like (9) or (12). The common type of discussion of molecules or solids in which one speaks of, say, an oxygen electron, an inner-shell electron, a bonding electron, a localized electron, a conduction electron, a  $\pi$  electron, or a  $\sigma$  electron actually implicitly presumes a set of equations like (9) or (12), since, of course, one cannot distinguish electrons and thus can never say that a particular electron is in some state that might, for instance, appear in some expansion of the many-electron wavefunction. Examples of such unjustified interpretations would be to think of the valence-bond wavefunction of a molecule as if there were an electron in each of the valence-bond orbitals moving independently of the others or to think of the electrons in the valence band of a semiconductor as if the states were the partially localized Wannier orbitals. Equations (9) or (12) do not imagine any such arbitrary assignment of real electrons to particular states. Rather, these equations are the result of approximating the exact many-electron wavefunction by a specific flexible type of function, which incorporates the necessary symmetry features, and then of varying the orbitals appearing in this function to minimize the energy, obtaining (9) or (12). Upon examining the resulting equations we note that each orbital is the eigenstate of

a one-electron operator which is identical with the Hamiltonian of a real electron moving in the potential of the nuclei and in a potential  $\hat{V}_i$ , where the potential  $\hat{V}_i$  is just an average potential (although perhaps a complicated average) which is really due to  $N-1$  electrons. In addition, this specific averaging of the potential due to the  $N-1$  other electrons is not done in an arbitrary way but is determined by the variational principle as that average which is consistent with the total many-electron wavefunction having the lowest possible total energy. Although it is true that all of these arguments, convincing as they are, do not rigorously prove that the self-consistent-field orbitals will be directly related to physical quantities and therefore of significance in themselves, it is clear that they do have some convenient properties. And in fact they have proved, in the case of the Hartree-Fock orbitals, to be of extreme usefulness in correlating a vast number of phenomena concerning atoms, molecules, and solids together into such a useful and self-consistent framework that for systems of electrons in the field of nuclei it is necessary for one to prove that these self-consistent-field orbitals are not useful for discussing some phenomenon, rather than that they are. Nevertheless, as discussed in II, the Hartree-Fock method seems incapable of discussing some very important problems of interest in studying bonding in molecules and solids, chemical reactions, and related topics. Many of these problems with the Hartree-Fock wavefunction center around the improper dissociation which occurs for many molecules and the resultant difficulty in abstracting quantities characteristic of and responsible for molecular formation. Part of this difficulty is due to not being able to move continuously between the molecular and atomic states in order to follow the changes which occur. The GF many-electron wavefunctions do dissociate properly as the nuclei are moved apart (see calculations on  $\text{H}_2$  and  $\text{LiH}$  in II and  $\text{Li}_2$  and  $\text{CH}_4$  in Sec. IV). Thus, we may now initiate a detailed study of these systems as the nuclei are brought together in order to examine how the various factors related to bonding vary and balance as the molecule is formed. In the next sections we will discuss the use and the significance of the orbital energies,  $\epsilon_{kk}$ .

### B. Koopmans' Theorem

In Appendix B we show that in general the energy of the  $N$ -electron system can be written as

$$E_N = A'_{N-1} + e_k, \quad (13a)$$

where  $e_k$  is the orbital energy for the  $k$  orbital. For the case where  $k$  is a  $b$  orbital, say  $kb$ , then  $A'_{N-1} = E_{N-1}$ , where  $E_{N-1}$  is the energy of the  $N-1$  electron GF wavefunction (of spin  $S_{N-1} = S_N + \frac{1}{2}$ ) with orbital  $kb$  removed. That is,

$$E_N = E_{N-1} + e_{kb}, \quad (13b)$$

and we obtain Koopmans' theorem<sup>6</sup> (see Appendix B). In the case of singlet states (13b) also holds for the  $ka$  orbitals.

### C. Selection of Occupied Orbitals

There is one point to note about Eqs. (8); if the size of the set of Roothaan basis functions is  $P$ , then the  $a$  and  $b$  equations each have  $P$  solutions. However, we need only  $n$   $a$ -type orbitals and  $m$   $b$ -type orbitals, so a method is required for selecting the occupied orbitals from the solutions to (8). The same problem occurs in the Hartree-Fock method, where for the case of all orbitals doubly-occupied only  $N/2$  orbitals of the  $P$  solutions to<sup>5</sup>

$$H_{\mu\nu}^{\text{HF}} C_{\nu i}^{\text{HF}} = S_{\mu\nu} C_{\nu i}^{\text{HF}} \epsilon_{ii}^{\text{HF}} \quad (14)$$

are needed. In both cases our criterion must be, of course, that we select that set of orbitals from Eqs. (8) or (14) which of all such sets yields the minimum total energy (if we are interested in the molecular ground state). Fortunately, it is not necessary to calculate the total energy for each selection of a set of occupied orbitals, since, for example, the state of lowest total energy for a GF wavefunction is obtained by selecting the  $n$  states of lowest orbital energy,  $\epsilon_{kk}^a$ , of (8a) and the  $m$  states of lowest orbital energy,  $\epsilon_{kk}^b$ , of (8b). [Similarly, for the (singlet) Hartree-Fock wavefunction, the state of lowest total energy is obtained by selecting the  $N/2$  orbitals of (14) with lowest orbital energy.] This follows immediately from (13). If  $N-1$  orbitals are fixed, then the lowest total energy is obtained if the  $N$ th orbital is chosen to be the lowest allowed unoccupied orbital. If  $N-p$  orbitals are fixed, then by successive applications of (13) the lowest total energy is obtained when the last  $p$  orbitals are chosen to be the lowest allowed unoccupied orbitals. Thus, for the lowest  $^2P$  state of  $B$ , we select at each iteration the lowest two  $s$  orbitals and the lowest  $p$  orbitals of the solutions of  $H^a$  and the lowest two  $s$  orbitals of  $H^b$ . For the second lowest  $^2P$  state of  $B$ , we select the  $s$  states as before but use the second lowest  $p$  orbital of  $H^a$ .

Acually the situation can be more complicated, especially for atoms where orbital degeneracies can be larger. In this case we need not always obtain the ground state of the system by placing the electrons in the lowest-lying orbitals. Thus, the Hartree-Fock energy of  $\text{Ti}^3\text{F}(4s^2 3d^2)$  is lower than that of  $\text{Ti}^3\text{D}(3d^4)$  even though  $\epsilon_{3d} < \epsilon_{4s}$ .<sup>7</sup> In such a case we solve for the lowest state of each configuration and compare energies to determine which is the ground state. Occasionally, slightly more complicated situations arise in the HF case. Thus, for large  $R$  the ground-state Hartree-Fock

wavefunction of BeH is obtained by putting two electrons in each of the first and third  $\sigma\text{HF}$  orbitals and one electron in the second.

There is another way in which one, in searching for the ground state, could conceivably obtain a self-consistent solution having too high an energy. This can occur when restrictions (e.g., spatial symmetry) are made upon the form of the orbitals which are not required by the form of the many-electron wavefunction. Thus, self-consistent orbitals could lead to a stationary point in the energy, but because of some restriction this stationary point is not an absolute minimum. Such a solution is said to be unstable.<sup>8</sup> For example, if one uses a Slater determinant but removes the restriction that the HF orbitals remain doubly occupied, then for both  $\text{H}_2$  and  $\text{LiH}$  the Hartree-Fock solutions are unstable for  $R$  greater than some critical value.<sup>9</sup> In the GI method there is no restriction comparable to that of doubly occupied orbitals, and thus if no restrictions are made concerning spatial symmetry, unstable solutions should normally not occur for atomic and molecular systems. However, if in solving the GF or HF equations one requires that the orbitals be symmetry functions, it is possible to obtain self-consistent solutions which are unstable (e.g., this would have occurred if in solving the GF equations for  $\text{H}_2$  or  $\text{Li}_2$  we had started with trial functions which were of  $\sigma_g$  and  $\sigma_u$  symmetry rather than just  $\sigma$  symmetry).

It is also possible that the variational equations could lead to a stationary point other than true minimum, not because of some symmetry restriction in the trial functions, but just because the trial function happened to be so close to this other stationary point that the solutions converged to it rather than the true minimum. If this were to occur one should probably find the energy increasing rather than decreasing as the solutions converge. So far as we are aware this had not happened for a GF or HF calculation.

We will now discuss some of the theoretical properties of GF wavefunctions.

## III. PROPERTIES OF GF WAVEFUNCTIONS

### A. Some Theorems on GF Wavefunctions

In II we used the variational principle to obtain the best possible orbitals  $\{\phi_{ia}\}$  and  $\{\phi_{ib}\}$  to use in  $G_f\Phi_{\text{prod}}\chi$ . Thus, we found that the orbitals have to be solutions of (5) or, equivalently, of (6):

$$\begin{aligned} \langle \delta_k \Phi | (H - E) \Theta O_{ff} | \Phi \rangle &= \langle \delta_k \Phi | H^{k,\text{GF}} | \Phi_k \rangle \\ &= \epsilon_{kk} \langle \delta_k \Phi | \Phi_k \rangle, \end{aligned} \quad (15)$$

which we can use to prove several interesting theorems.

<sup>8</sup> D. J. Thouless, *The Quantum Mechanics of Many-Body Systems* (Academic Press Inc., New York, 1961).

<sup>9</sup> C. A. Coulson and I. Fischer, *Phil. Mag.* **40**, 386 (1949); W. H. Adams, *J. Chem. Phys.* **37**, 2009 (1962).

<sup>6</sup> T. Koopmans, *Physica* **1**, 104 (1934).

<sup>7</sup> R. E. Watson, *Phys. Rev.* **119**, 1934 (1960); *Tech. Rept. No. 12, Solid State and Molecular Theory Group, MIT* (1959).

### 1. The Hellmann-Feynman Theorem

Let  $\lambda$  be some parameter of the Hamiltonian of the system and take the variation on the total energy for the GF wavefunction

$$E = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle,$$

where  $\psi = G_f \Phi \chi$ . We obtain

$$\begin{aligned} \partial E / \partial \lambda = & \langle \psi | \psi \rangle^{-1} (\langle \psi | \partial H / \partial \lambda | \psi \rangle + \langle \partial \psi / \partial \lambda | H | \psi \rangle \\ & + \langle \psi | H | \partial \psi / \partial \lambda \rangle - E \langle \partial \psi / \partial \lambda | \psi \rangle - E \langle \psi | \partial \psi / \partial \lambda \rangle). \end{aligned} \quad (16)$$

But from (15) of I,

$$\frac{\langle \partial \psi / \partial \lambda | H - E | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\langle \partial \Phi / \partial \lambda | (H - E) \Theta O_{ff} | \Phi \rangle}{\langle \Phi | \Theta O_{ff} \Phi \rangle}.$$

We now expand

$$\frac{\partial \Phi}{\partial \lambda} = \sum_{k=1}^N \Phi_k \frac{\partial \phi_k}{\partial \lambda}, \quad (17)$$

where  $\Phi_k$  is the same as  $\Phi$  but with orbital  $\phi_k$  deleted. Thus, using (15),

$$\begin{aligned} \langle \partial \Phi / \partial \lambda | (H - E) \Theta O_{ff} | \Phi \rangle &= \sum_{k=1}^N \langle \partial \phi_k / \partial \lambda | H^{k,GF} | \phi_k \rangle \\ &= \sum_{k=1}^N \epsilon_{kk} \langle \partial \phi_k / \partial \lambda | \phi_k \rangle, \end{aligned}$$

and the last four terms in (16) yield

$$\begin{aligned} \sum_{k=1}^N \epsilon_{kk} (\langle \partial \phi_k / \partial \lambda | \phi_k \rangle + \langle \phi_k | \partial \phi_k / \partial \lambda \rangle) \\ = \sum_{k=1}^N \epsilon_{kk} (\partial / \partial \lambda) \langle \phi_k | \phi_k \rangle, \end{aligned}$$

which is zero since each orbital is normalized. Hence, we obtain

$$\frac{\partial E}{\partial \lambda} = \frac{\langle \psi | \partial H / \partial \lambda | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\langle \Phi | \partial H / \partial \lambda | \Theta O_{ff} \Phi \rangle}{\langle \Phi | \Theta O_{ff} \Phi \rangle},$$

the Hellmann-Feynman theorem for GF wavefunctions. The key relation for this theorem is (15), which is satisfied only because we have used the variational theorem to functionally optimize our wavefunction. Relation (15) also holds for the GFR equations where

$$\delta \phi_k = \sum_{\mu=1}^M X_{\mu} (\delta C_{\mu k}),$$

but in this case we do not have

$$\frac{\partial \phi_k}{\partial \lambda} = \sum_{\mu=1}^M X_{\mu} \frac{\partial C_{\mu k}}{\partial \lambda},$$

because even though  $\phi_k$  is expanded in terms of the  $M$ -dimensional basis this does not imply that  $\partial \phi_k / \partial \lambda$  can be expanded in the same basis, since the basis set

is not complete. Thus the Hellmann-Feynman theorem holds for the GF wavefunction but not for the GFR wavefunction.

### 2. One-Electron Perturbations

Consider the Hamiltonian  $H = H^{(0)} + H^{(1)}$ , where  $H^{(0)}$  is the zero-order Hamiltonian, say (1), and the perturbation  $H^{(1)}$  involves only one-electron operators. Expanding the total wavefunction  $\psi$  as  $\psi^{(0)} + \psi^{(1)} + \dots$ , we obtain

$$\begin{aligned} E &= \frac{\langle \psi^{(0)} + \psi^{(1)} + \dots | H | \psi^{(0)} + \psi^{(1)} + \dots \rangle}{\langle \psi^{(0)} + \psi^{(1)} + \dots | \psi^{(0)} + \psi^{(1)} + \dots \rangle} \\ &= \langle 0 | H | 0 \rangle / \langle 0 | 0 \rangle + \langle 0 | 0 \rangle^{-1} \\ &\quad \times (\langle 1 | H - E | 0 \rangle + \langle 0 | H - E | 1 \rangle) + \dots \end{aligned}$$

Thus, the first-order term in  $E$  is

$$\begin{aligned} E^{(1)} &= \langle 0 | H^{(1)} | 0 \rangle / \langle 0 | 0 \rangle + \langle 0 | 0 \rangle^{-1} \\ &\quad \times (\langle 1 | H^{(0)} - E^{(0)} | 0 \rangle + \langle 0 | H^{(0)} - E^{(0)} | 1 \rangle). \end{aligned} \quad (18)$$

Now if  $\psi^{(0)}$  is the *exact* eigenfunction of  $H^{(0)}$ , then the bracketed term in Eq. (18) is zero, and we obtain the usual form for  $E^{(1)}$ . But if  $\psi^{(0)}$  is only an approximate wavefunction, then in general all terms remain. However, we will now show that for GF wavefunctions the bracketed term in (18) is indeed zero. We take  $\psi^{(0)} \equiv G_f \Phi^0 \chi$  to be the GF wavefunction for  $H^{(0)}$ , with orbitals  $\phi_j^{(0)}$ . We expand  $\phi_j = \phi_j^{(0)} + \phi_j^{(1)} + \dots$ ; thus the first-order wavefunction is

$$\psi^{(1)} = \sum_{j=1}^N \psi_j^{(1)},$$

where  $\psi_j^{(1)} = G_f \Phi_j^{(1)} \chi$  has the  $\phi_j^{(0)}$  ground-state orbital replaced by  $\phi_j^{(1)}$ . Then, just as in Sec. III.A.1 above we use (15) to obtain

$$\begin{aligned} \langle 1 | H^{(0)} - E^{(0)} | 0 \rangle + \langle 0 | H^{(0)} - E^{(0)} | 1 \rangle \\ = \sum_j \epsilon_{jj} (\langle \phi_j^{(1)} | \phi_j^{(0)} \rangle + \langle \phi_j^{(0)} | \phi_j^{(1)} \rangle). \end{aligned}$$

But we require that  $\phi_j$  and  $\phi_j^{(0)}$  be normalized; hence,

$$\langle \phi_j^{(1)} | \phi_j^{(0)} \rangle + \langle \phi_j^{(0)} | \phi_j^{(1)} \rangle = 0.$$

Thus,

$$E^{(1)} = \langle 0 | H^{(1)} | 0 \rangle / \langle 0 | 0 \rangle. \quad (19)$$

That is, we obtain the first-order properties by just evaluating the expectation value in terms of the zero-order GF wavefunction. We could have obtained this result more formally by putting in a perturbation parameter  $\lambda$  and using the Hellmann-Feynman theorem.

If all the orbitals  $\{\phi_j^{(0)}\}$  and  $\{\phi_j^{(1)}\}$  are expanded in the same finite basis set and if the  $\phi_j^{(0)}$  are the GFR orbitals for  $H^{(0)}$ , then we again obtain (19).

Note that throughout this section  $H^{(0)}$  is the complete unperturbed Hamiltonian, Eq. (1). It is *not* some truncated Hamiltonian of which  $\psi^{(0)}$  is the eigenfunction.

### 3. Singly Excited Configurations

From I we can expand the exact wavefunction as a sum over  $G_f\gamma$  configurations,

$$\psi_{\text{exact}} = \sum_{j_1, j_2, \dots, j_N} C_{j_1, \dots, j_N} G_f\gamma [\phi_{j_1}(1) \phi_{j_2}(2) \cdots \phi_N(N) \chi],$$

where the  $\{\phi_j(1)\}$ ,  $\{\phi_j(2)\}$ ,  $\dots$ , are each complete orthogonal sets. Let us take the GF wavefunction as one term, the basic one, in this expression and consider the singly excited configurations (i.e., ones which have one GF orbital, say  $k$ , replaced by an excited orbital, say  $k'$ ). Denote the GF wavefunctions as  $|0\rangle$  and let  $|1\rangle$  be the sum over all first-order terms,

$$|1\rangle = \sum_{j=1}^N C_j G_f\gamma(\Phi_j \chi),$$

where  $\Phi_j$  has the  $j$ th GF orbital,  $\phi_j$ , replaced by a linear combination over all excited orbitals,  $\phi_j'$ . Then, from (18) the first-order change in energy is

$$E^{(1)} = (\langle 1 | H - E | 0 \rangle + \langle 0 | H - E | 1 \rangle) / \langle 0 | 0 \rangle,$$

and from (15)

$$\langle 1 | H - E | 0 \rangle = \sum_{j=1}^N \epsilon_{jj} \langle \phi_j' | \phi_j \rangle.$$

But  $\phi_j'$  is orthogonal to  $\phi_j$ ; hence,

$$E^{(1)} = 0.$$

This result, that the total energy is stationary with respect to first-order changes in the wavefunction is, of course, equivalent to the variation condition and is sometimes called the Brillouin theorem.

### 4. The Cusp Conditions

Consider the GI equations for an atom; all of the terms are bounded near the nucleus except  $\hbar\phi_k = [-\frac{1}{2}\nabla^2 - (Z/r)]\phi_k$ . In order for this term to be finite at the nucleus, the  $\phi_k$  must satisfy the cusp condition  $f'/f = -Z/(l+1)$ , where  $\phi_k = f(R)r^l Y_{lm}(\Theta, \Phi)$ , just as in the Hartree-Fock case.<sup>10</sup> This condition applies to the exact GI orbitals and not to the finite basis set solutions; hence, it forms a test of whether the basis set is adequate.

### 5. The Virial Theorem

For any approximate wavefunction, if the basis functions and internuclear distances are scaled to yield a stationary energy, the Virial theorem for equilibrium,<sup>11</sup>

<sup>10</sup> C. C. J. Roothaan and A. W. Weiss, Rev. Mod. Phys. **32**, 194 (1960).

<sup>11</sup> J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Co., New York, 1963), p. 34; P.-O. Löwdin, J. Mol. Spectry. **3**, 46 (1959).

$2T + V = 0$ , will be satisfied. This holds for GF wavefunctions with any number of basis functions.

## 6. Discussion

The results obtained in Secs. III.A.1-5 above apply equally well to all GI wavefunctions and also to other functionally optimized wavefunctions such as those obtained from the Hartree-Fock method.<sup>12-14</sup>

Question is sometimes raised as to whether the energy is the best criterion for optimizing a wavefunction (as opposed to optimizing some property, e.g., the dipole moment). We see here, especially in Secs. III.A.1 and 2, an important example of the deep significance of using the energy for the criterion (a more obvious reason is that we always obtain an upper bound for the energy, and therefore improving the energy may mean improving the wavefunction, and therefore in the limit improving most other properties).

## B. Spatial Symmetry

### 1. Homonuclear Diatomic Molecules

As discussed in II the Hamiltonian (1) is generally invariant under some group,  $G$ , of spatial transformations; hence, the exact many-electron eigenfunction of (1) can be required to be a symmetry function<sup>15</sup> of the group  $G$ . Since we want our approximate wavefunction,  $G_f\gamma\Phi\chi$ , to have as nearly as possible the same behavior as the exact wavefunction, we will require that the  $G_f\gamma\Phi\chi$  also be a symmetry function for  $G$ . In general, such a requirement places restrictions on the orbitals in  $\Phi$  if we are to retain a single  $G_f\gamma\Phi\chi$  with  $\phi$  as a product of orbitals. We will now examine these restrictions for some typical  $G$ . We will take the total spin to be zero and require that the many-electron wavefunction be nondegenerate and totally symmetric (many molecular ground states satisfy these conditions).

From Appendix C of II, if  $G_f\gamma\Phi\chi$  is nondegenerate, the space spanned by the orbitals in  $\Phi$  is invariant under the transformations of  $G$ . In Appendix A of III we showed that  $O_r\gamma\Phi$  transforms to  $(\det U)O_r\gamma\Phi'$  [and hence  $G_f\gamma\Phi\chi$  transforms to  $(\det U)G_f\gamma\Phi'\chi$ ] under any unitary transformation,  $U$ , of the  $a$  set or of the  $b$  set of orbitals among themselves. We show in Appendix A that any permutation which interchanges the  $a$  set and the  $b$  set of orbitals leaves  $G_f\gamma\Phi\chi$  invariant. Hence, in order that  $G_f\gamma\Phi\chi$  be totally symmetric it is sufficient that each transformation of  $\Phi$  correspond either to (i) a unitary transformation,  $U_a$ , of the  $a$  set of orbitals among themselves and a unitary transformation,  $U_b$  of

<sup>12</sup> J. C. Slater, *Quantum Theory of Molecules and Solids* (McGraw-Hill Book Co., New York, 1963).

<sup>13</sup> R. E. Stanton, J. Chem. Phys. **36**, 1298 (1962).

<sup>14</sup> R. K. Nesbet, Advan. Chem. Phys. **9**, 321 (1965), see p. 330.

<sup>15</sup> By symmetry function we mean a basis function of an irreducible representation of the symmetry group.

the  $b$  set among themselves with  $(\det U^a)(\det U^b) = +1$ ; (ii) a permutation such that the  $a$  set of orbitals is taken into the  $b$  set and vice versa; or (iii) a combination of (i) and (ii). Although we do not show that it is necessary that one of these conditions must apply in order for  $G_f\Phi\chi$  to be a symmetry function, we will see that the conditions are broad enough that such  $G_f\Phi\chi$  can be constructed for most molecules.

In II we showed the GF wavefunction for  $H_2$  is

$$G_f[\phi_a(1)\phi_b(2)\alpha(1)\beta(2)],$$

where  $\phi_a$  is peaked near one proton and  $\phi_b$  is symmetrically related and peaked near the other, and we found that  $\phi_a$  and  $\phi_b$  each become ground-state hydrogen orbitals as the internuclear distance,  $R$ , is increased. Similarly, as reported below in Sec. IV the GF wavefunction for  $Li_2$  is

$$G_f(\phi_{1a}\phi_{2a}\phi_{3a}\phi_{1b}\phi_{2b}\phi_{3b}\alpha\alpha\beta\beta),$$

where  $\phi_{1a}$  and  $\phi_{1b}$  are essentially Li 1s orbitals on the left center,  $\phi_{2a}$  and  $\phi_{2b}$  are essentially Li 1s orbitals on the right center, and  $\phi_{3a}$  and  $\phi_{3b}$  are orbitals with significant amplitudes on both centers, but with higher amplitudes on the left and right centers, respectively. The spatial symmetry group is  $D_{\infty h}$  and each orbital is a  $\sigma$  orbital, i.e., is left invariant under  $C_{\infty v}$ . But under the horizontal mirror interchanging the nuclei,  $\sigma_h$ ,

$$\phi_{1a} \leftrightarrow \phi_{2b},$$

$$\phi_{2a} \leftrightarrow \phi_{1b},$$

$$\phi_{3a} \leftrightarrow \phi_{3b}.$$

Thus, the many-electron wavefunction is invariant under  $D_{\infty h}$ , although the GF orbitals are symmetry functions for  $C_{\infty v}$ . It is clear that as the internuclear distance,  $R$ , increases to infinity the orbitals charge continuously into the orbitals for free Li atoms, and thus that the GF wavefunction for  $Li_2$  dissociates properly.

The above results are typical for singlet states of homonuclear molecules. As a more complicated example, consider  $N_2$  and try to describe it as follows (where the use of A or B implies that the orbital has a higher amplitude in the region of the A or B nucleus): two localized 1s-type orbitals on each center 1sA1, 1sA2, 1sB1, 1sB2; two pairs of localized 2s-type orbitals 2sA1, 2sA2, 2sB1, 2sB2; a pair of states  $\sigma A1, \sigma B1$  which correspond to a  $\sigma$  bond; and two pairs of states  $\pi Ax, \pi Bx, \pi Ay, \pi By$  which correspond to the two  $\pi$  bonds. Under the transformations of  $C_{\infty v}$  let all states be invariant except for the  $\pi$  states, for which we let  $\pi Ax$  and  $\pi Ay$  transform among themselves and  $\pi Bx$  and  $\pi By$  transform among themselves ( $\det U_a = \det U_b = +1$  for proper rotations,  $= -1$  for improper rotations). Let the states transform the following way under  $\sigma_h$

(the reflection which interchanges the nuclei):

$$1sA1 \leftrightarrow 1sB1,$$

$$1sA2 \leftrightarrow 1sB2,$$

$$2sA1 \leftrightarrow 2sB1,$$

$$2sA2 \leftrightarrow 2sB2,$$

$$\sigma A1 \leftrightarrow \sigma B1,$$

$$\pi Ax \leftrightarrow \pi Bx,$$

$$\pi Ay \leftrightarrow \pi By, \quad (20)$$

and write  $G_f\Phi\chi$  with

$$\Phi = \phi_{1sA1}\phi_{1sB2}\phi_{2sA1}\phi_{2sB2}\phi_{\sigma A1}\phi_{\sigma B1}\phi_{\pi Ax}\phi_{\pi Ay}\phi_{1sB1} \\ \times \phi_{1sA2}\phi_{2sB1}\phi_{2sA2}\phi_{\sigma B1}\phi_{\pi Bx}\phi_{\pi By}.$$

The specific choice of which orbitals of (20) correspond to the  $a$  set and which to the  $b$  set was made in order to allow the states to have the significance proposed for them; e.g., if 1sA1 and 1sA2 are to both be like free atom 1s states (although somewhat split), then we expect them to have nonzero (actually a large) overlap with each other which precludes them from both being in the same antisymmetric set; similarly, we put 2sA1 and 2sA2 in different sets. On the other hand,  $\pi Ax$  and  $\pi Ay$  must be in the same set, since they transform into each other under  $C_{\infty v}$ . In the Hartree-Fock method we would have had seven doubly occupied orbitals:  $1\sigma_g$  and  $1\sigma_u$  to describe what are primarily  $N$  1s electrons (note that with the Hartree-Fock method even the states representing the inner-shell 1s states are delocalized<sup>16</sup>),  $2\sigma_g$ ,  $3\sigma_g$ , and  $2\sigma_u$ , which are bonding and nonbonding pairs, and  $1\pi_{ux}$  and  $1\pi_{uy}$ , which are  $\pi$  bonding pairs. Hence the GF method allows the inner-shell and nonbonding pairs to be properly described as localized states, whereas the Hartree-Fock method cannot, and the GF method allows each of the three bonding orbitals to split so as to account for left-right correlations. It is clear then, since each orbital is more concentrated on one center than the other, that as the internuclear distance increases this concentration will increase in a continuous manner until at  $R = \infty$  each  $N$  contains completely localized atomic states. Thus, the GF method admits a quite reasonable description

<sup>16</sup> One may take a unitary transformation of the HF orbitals to obtain new more localized orbitals [e.g., for  $N_2$  we could transform to  $\phi'_1 = (1/\sqrt{2})(\phi_{1\sigma_g} + \phi_{1\sigma_u})$  and  $\phi'_2 = (1/\sqrt{2})(\phi_{1\sigma_g} - \phi_{1\sigma_u})$ , both of which are quite localized]. The Slater determinant wavefunction using these new orbitals is equivalent to the old one and leads to the same expectation values. However, as discussed in Paper II, the new orbitals are not eigenfunctions of the Hartree-Fock Hamiltonian [ $H_{HF}$  of Eq. (9)] and thus cannot be given the independent particle interpretation. T. L. Gilbert [in *Molecular Orbitals in Chemistry, Physics and Biology*, P.-O. Löwdin and G. Pullman, Eds. (Academic Press Inc., New York, 1964), p. 409] and W. H. Adams [J. Chem. Phys. 37, 209 (1962)] have presented methods for solving for localized Hartree-Fock orbitals directly.

of the wavefunction in such a way that the wavefunction dissociates properly.

## 2. General Considerations

We must now consider some general points about the spatial symmetry of the GF orbitals. There are just two 1-electron Hamiltonians,  $H^a$  and  $H^b$ , involved; all of the  $\phi_{ia}$  GF orbitals are eigenfunctions of  $H^a$ , and all of the  $\phi_{ib}$  GF orbitals are eigenfunctions of  $H^b$ . Since the  $H^a$  is invariant under any unitary transformation of the  $a$  orbitals among themselves and the  $b$  orbitals among themselves,  $H^a$  commutes with any of the symmetry transformations of  $\mathcal{G}$  which result in such a transformation. The set of all such transformations forms a group,  $\mathcal{G}'$ , which is a subgroup of  $\mathcal{G}$ . The  $\mathcal{G}'$  for  $H^a$  and  $H^b$  are the same, since the transformations of  $\mathcal{G}$  which are not in  $\mathcal{G}'$  are those which take the  $a$  set of orbitals into the  $b$  set and vice versa, and hence are not in  $\mathcal{G}'$  and conversely. Since  $H^a$  and  $H^b$  commute with the elements of  $\mathcal{G}'$ , the eigenfunctions of  $H^a$  and  $H^b$  (i.e.,  $\{\phi_{ia}\}$  and  $\{\phi_{ib}\}$ ) are symmetry functions of  $\mathcal{G}'$ . In the case of diatomic molecules (homonuclear and heteronuclear), we saw from the examples of  $\text{H}_2$ ,  $\text{Li}_2$ , and  $\text{N}_2$  that the orbitals can be taken as eigenfunctions of  $\mathcal{C}_{\infty v}$  (e.g.,  $\sigma$  and  $\pi$  orbitals).

If  $g \in \mathcal{G}$  and  $g' \in \mathcal{G}'$  then we can write  $g = g_1' g_{ab} = g_{ab} g_2'$ , where  $g_1', g_2' \in \mathcal{G}'$ , and  $g_{ab}$  is a symmetry transformation which takes all  $a$  orbitals into  $b$  orbitals and vice versa. Thus,  $g^2 = g_1' g_{ab} g_1' g_{ab} = g_1' g_2' g_{ab} g_{ab} = g_1' g_2'$ . Hence, the kernel of the homomorphism of  $\mathcal{G}$  onto  $\mathcal{G}'$  contains only elements of order 2 and thus is of even order. This leads to no great problems for homonuclear molecules, where we saw that  $\mathcal{G} = \mathcal{D}_{\infty h}$  and  $\mathcal{G}' = \mathcal{C}_{\infty v}$  are allowed, corresponding to a kernel of four elements. However, for some symmetries, especially those containing symmetry transformations which interchange nuclei and are of order greater than two, it may occur that  $\mathcal{G}' = \mathcal{G}$ .

TABLE I. The GF orbitals for  $\text{Li}_2$ ,  $R = 5.051a_0$ .  $\phi_{ib}$  is obtained from  $\phi_{ia}$  by interchanging A and B. The  $z$  axis on each center points toward the other center. The basis functions are Slater orbitals with orbital exponents  $\zeta$ .

	$\zeta$	$\phi_{1a}$	$\phi_{2a}$	$\phi_{3a}$
A1s	2.26431	0.90585	-0.00292	-0.17315
A1s	4.471	0.17752	-0.00055	-0.01392
A2s	0.66543	0.00280	0.00279	1.00161
A3s	2.75168	-0.08993	0.00057	-0.00898
A2p	0.77642	-0.00238	0.00176	0.12366
B1s	2.26431	0.00279	0.88872	-0.06545
B1s	4.471	0.00040	0.15550	-0.00635
B2s	0.66543	0.00216	-0.00950	0.01485
B3s	2.75168	-0.00045	-0.03137	-0.02444
B2p	0.77642	0.00139	-0.00317	0.03523
Orbital energy		-2.5027	-2.4443	-0.2135

TABLE II. Energies for  $\text{Li}_2$ .

	NBF	$R = 5.051$	$R = \infty$	Sep atoms
HF	6	-14.84149 <sup>a</sup>	-14.72877 <sup>b</sup>	-14.83696 <sup>c</sup>
GF	6	-14.84970 <sup>d</sup>	-14.83696 <sup>e</sup>	-14.83696 <sup>e</sup>
HF	10	-14.87118 <sup>f</sup>	-14.75568 <sup>g</sup>	-14.86542 <sup>h</sup>
GF	10	-14.87977 <sup>i</sup>	-14.86561 <sup>j</sup>	-14.86561 <sup>j</sup>

<sup>a</sup> R. J. Ransil, Rev. Mod. Phys. **32**, 245 (1960).

<sup>b</sup> Optimum orbital exponents:  $\zeta_{1s} = 2.6903$ ,  $\zeta_{2s} = 0.5658$ .

<sup>c</sup> E. Clementi and D. L. Raimondi, J. Chem. Phys. **38**, 2686 (1963).

<sup>d</sup> Optimum orbital exponents:  $\zeta_{1s} = 2.6901$ ,  $\zeta_{2s} = 0.6534$ ,  $\zeta_{2p} = 0.812$ .

<sup>e</sup> Optimum orbital exponents:  $\zeta_{1s} = 2.6906$ ,  $\zeta_{2s} = 0.6396$ .

<sup>f</sup> Stevens and Lipscomb, Ref. 19.

<sup>g</sup> Optimum orbital exponents:  $\zeta_{1s} = 2.145$ ,  $\zeta_{1s} = 4.286$ ,  $\zeta_{2s} = 0.5731$ ,  $\zeta_{2p} = 2.590$ .

<sup>h</sup> Optimum orbital exponents:  $\zeta_{1s} = 2.128$ ,  $\zeta_{1s} = 4.279$ ,  $\zeta_{2s} = 0.6687$ ,  $\zeta_{2p} = 2.590$ .

<sup>i</sup> See Table I.

<sup>j</sup> Orbital exponents the same as in Footnote h.

For example, for  $\text{CH}_4$  we have  $\mathcal{G} = \mathcal{T}_d$ , and  $\mathcal{G}'$  is also  $\mathcal{T}_d$ , which means that the GF orbitals have  $T_d$  symmetry and hence do not localize. Another example is benzene, where  $\mathcal{G} = \mathcal{D}_{6h}$  and  $\mathcal{G}'$  can be  $\mathcal{D}_{3h}$ ; that is, the GF orbitals can have alternate character but are not completely localized.

We should point out that the GF wavefunction is left essentially invariant under any transformation of the  $a$  orbitals among themselves and similarly for the  $b$  orbitals. Hence, one may transform the GF orbitals to more localized form just as Wannier, Lennard-Jones, Ruedenberg, and others<sup>17</sup> have suggested for the Hartree-Fock orbitals. However, in both cases the new orbitals lead to off-diagonal Lagrange multipliers and hence cannot be given a rigorous independent particle interpretation.

Note that as discussed in II one could use  $\Phi\Phi$ , a projected wavefunction, rather than a single product of orbitals  $\Phi$ , in which case, one could get even lower energies and remove some of the restrictions on the orbitals. However, in this case one has different equations to solve for different symmetries, and one need not obtain an individual particle interpretation of the best orbitals. One could also just ignore the spatial symmetry requirements in finding the best  $G_f\Phi\chi$ . The disadvantage here is that the interpretation of the results in terms of physically meaningful quantities is less certain. Of course, any problems with spatial symmetry that occur in the GF method also occur in the Hartree-Fock and UHF methods, but the converse is *not* true (e.g.,  $\text{H}_2$ ,  $\text{Li}_2$ , and  $\text{N}_2$ ).

<sup>17</sup> G. H. Wannier, Phys. Rev. **52**, 191 (1937); J. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 1, 14 (1949); J. A. Pople, Quart. Rev. **11**, 273 (1957); C. Edmiston and K. Ruedenberg, Rev. Mod. Phys. **35**, 457 (1963).

TABLE III. The GF orbitals for  $\text{CH}_4$ ,  $R=2.05a_0$ . The H nuclei are at the alternate vertices of a cube, and the coordinate axes are perpendicular to the faces of the cube. The orbitals  $\phi_{4a}$ ,  $\phi_{4b}$ , and  $\phi_{4c}$  have  $t_{2y}$  and  $t_{2z}$  symmetry, respectively, with coefficients as given for  $\phi_{3a}$ ,  $\phi_{3b}$ . The GF orbital symmetries are given in parentheses. The orbital exponents used here are optimum for the Hartree-Fock wavefunction [R. M. Pitzer, J. Chem. Phys. **46**, 4871 (1967)].

	$\zeta$	$\phi_{1a}$ ( $a_1$ )	$\phi_{2a}$ ( $a_1$ )	$\phi_{1b}$ ( $a_1$ )	$\phi_{2b}$ ( $a_1$ )
H1s	1.17	-0.00670	0.06744	-0.00279	0.30549
C1s	5.68	0.99322	-0.25943	0.99575	-0.16467
C2s	1.76	0.03335	0.88744	0.01955	0.28193
Orbital energy		-11.2991	-1.0830	-11.2236	-0.9569
		$\phi_{2b}$ ( $t_{2x}$ )	$\phi_{3a}$ ( $t_{2x}$ )		
H1s	1.17	0.16546	0.44958		
C2px	1.76	0.79699	0.28659		
Orbital energy		-0.6451	-0.6309		

#### IV. CALCULATIONS

##### A. The $\text{Li}_2$ Molecule

In order to further demonstrate the correct dissociation and the symmetry of the GF wavefunctions, we will describe some results on  $\text{Li}_2$ . The GF wavefunction is

$$G_f(\phi_{1a}\phi_{2a}\phi_{3a}\phi_{1b}\phi_{2b}\phi_{3b}\alpha\alpha\alpha\beta\beta\beta),$$

where  $\phi_{1a}\phi_{2a}\phi_{1b}$  and  $\phi_{2b}$  are essentially Li 1s orbitals and  $\phi_{3a}$  and  $\phi_{3b}$  form a bonding pair of orbitals. The Hartree-Fock wavefunction is

$$\alpha(\phi_1\phi_2\phi_3\phi_1\phi_2\phi_3\alpha\alpha\alpha\beta\beta\beta),$$

where  $\phi_1$  and  $\phi_2$  are essentially symmetric and anti-symmetric combinations of Li 1s orbitals and  $\phi_3$  is a bonding orbital. The calculations<sup>18</sup> used Slater-orbital basis sets and were carried out for  $R=R_e$  and  $R=\infty$ ; the orbital exponents used are optimum for the Hartree-Fock wavefunctions.<sup>19</sup> The GF orbitals for  $R=R_e$  are tabulated in Table I, the  $\phi_{3a}$  orbitals for both  $R$  are shown in Fig. 1, and the  $\phi_3$  orbitals for both  $R$  are compared to the corresponding orbital of Li in Fig. 2. Thus

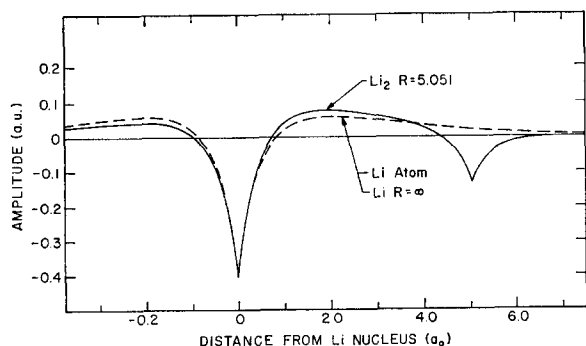


FIG. 1. GF orbitals for  $\text{Li}_2$  and Li.

<sup>18</sup> The Nesbet-Stevens diatomic program was used for all integrals of  $\text{Li}_2$  except for the one-center two-electron integrals.

<sup>19</sup> The Hartree-Fock wavefunctions for  $\text{Li}_2$  are reported by R. M. Stevens and W. N. Lipscomb, J. Chem. Phys. **42**, 4302 (1965).

we see that the bonding orbitals of  $\text{Li}_2$  are very similar to the atomic orbitals, except that a small amount of hybridization occurs, and a subsidiary 2s peak comes from the other center. Such a cogent description of bonding does *not* arise from the Hartree-Fock wavefunctions.

The energies from these calculations are compared in Table II. From Table II and Fig. 1 we see that the GF method treats the free atoms and molecules in a consistent manner, whereas the Hartree-Fock method does not. The use of Koopmans' theorem leads to the following predictions of first ionization potential: 4.95 eV for the Hartree-Fock case, and 5.81 eV for the GF case. This is to be compared to the experimental value of 4.96 eV. On the other hand, the predicted dissociation energies are 0.12 eV for the Hartree-Fock case and 0.35 eV for the GF case as compared to the experimental value of  $D_e=1.05$  eV.

##### B. The $\text{CH}_4$ Molecule

In order to demonstrate the dissociation of GF wavefunctions for polyatomic molecules, we report some calculations<sup>20</sup> on methane. Two configurations were considered: (i) The tetrahedral molecule at  $R=2.05a_0$  (the

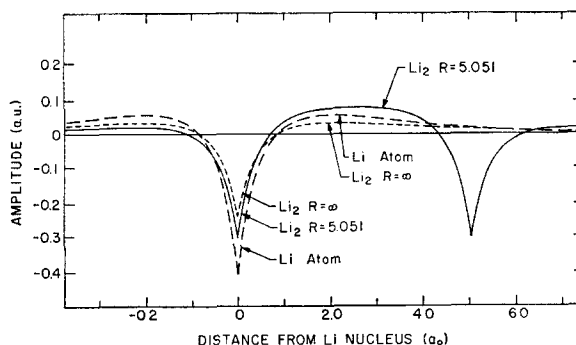


FIG. 2. Hartree-Fock orbitals for  $\text{Li}_2$  and  $\text{Li}$ .

<sup>20</sup> The MIT-Harvard Polyatomic integral program for Slater orbitals [e.g., see W. E. Palke and W. N. Lipscomb, J. Am. Chem. Soc. **88**, 2384 (1966)] was used for all integrals of  $\text{CH}_4$  and  $\text{CH}_3$ .



TABLE IV. The GF orbitals for planar  $\text{CH}_3$ ,  $R=2.039a_0$ . The molecule is in the  $xy$  plane with the origin at the C and one H nucleus on the  $x$  axis. The orbitals  $\phi_{4a}$ ,  $\phi_{4b}$  are of  $e_y$  symmetry and related to  $\phi_{3a}$ ,  $\phi_{3b}$  by a  $90^\circ$  rotation.

	$\zeta$	$\phi_{1a}$ ( $a_1$ )	$\phi_{2a}$ ( $a_1$ )	$\phi_{1b}$ ( $a_1$ )	$\phi_{2b}$ ( $a_1$ )
H1s	1.203	-0.00553	0.13341	-0.00275	0.35439
C1s	5.673	0.99363	-0.26115	0.99585	-0.18160
C2s	1.82	0.02749	0.81800	0.01742	0.37586
Orbital energy		-11.2363	-1.0101	-11.1643	-0.8180
	$\zeta$	$\phi_{3a}$ ( $e_x$ )	$\phi_{3b}$ ( $e_x$ )		
H1s	1.203	0.29302	0.53885		
C2px	1.67	0.71263	0.39613		
Orbital energy		-0.5837	-0.5639		
	$\zeta$	$\phi_{3a}$ ( $e_x$ )			
C2pz	1.67	1.0			
Orbital energy		-0.3963			

experimental  $R_e$  is 2.0508), and (ii) the dissociated molecule with one H at  $\infty$  and the remaining  $\text{CH}_3$  in the planar configuration with  $R=2.039a_0$  (the experimental  $R_0$  for  $\text{CD}_3$ ). The GF orbitals for (i) are in Table III and the GF orbitals for (ii) are in Table IV. Note the large splittings in the bonding orbitals. The energies are shown in Table V, where again we note that the GF wavefunctions dissociate properly (the HF wavefunction goes to  $\text{CH}_3^+ + \text{H}^-$  as one proton is pulled off of  $\text{CH}_4$ ). Such correct behavior is crucial in order to hope to consider chemical reactions.

### C. Correlation

Correlation energy has usually been defined as the difference between the exact energy and the HF energy. Such a definition becomes ludicrous for large  $R$ , since the limit of the HF energy of a molecule as  $R \rightarrow \infty$  is usually much larger than the sum of the HF energies for the separated atoms. We will call the portion of the correlation energy due to this bad dissociation of HF wavefunctions the *artificial correlation energy*, since it is purely an artifact of the HF method (due to the orbitals all being orthogonal and thus often doubly occupied) and has no physical significance whatsoever. The artificial correlation energy at  $R = \infty$  (the only point at which it is well defined) for several molecules is shown in Table VI; the artificial correlation energy is

TABLE V. Energies for  $\text{CH}_4$  and for  $\text{CH}_3 + \text{H}$ . The HF wavefunction for  $\text{CH}_4$  dissociates to  $\text{CH}_3^+ + \text{H}^-$  as  $R \rightarrow \infty$ .

	$\text{CH}_4$	$\text{CH}_3 + \text{H}$ $R \rightarrow \infty$	$\text{CH}_3 + \text{H}$ Separately
HF	-40.12822 <sup>a</sup>	-39.63972 <sup>d</sup>	-39.96734 <sup>d</sup>
GF	-40.17066 <sup>b</sup>	-39.98895 <sup>c</sup>	-39.98895 <sup>c</sup>

<sup>a</sup> R. M. Pitzer, J. Chem. Phys. **46**, 4871 (1967).

<sup>b</sup> Using the wavefunction in Table III.

<sup>c</sup> Using the wavefunction in Table IV.

<sup>d</sup> Using the basis set in Table IV.

generally about twice the bond energy. Since there seems to be no way to calculate this artifactual correlation energy as a function of  $R$  and thus to correct the HF correlation energies in order to obtain just the physically significant part, we must look elsewhere for a way to find the "true" correlation energy.

Since the GF wavefunctions do not contain correlation (each orbital is determined by the *average* field due to all the other orbitals) and since the GF wavefunctions do dissociate correctly, the GF energy forms a satisfactory datum with respect to which to define correlation.

### V. PERTURBATION SCHEMES

There have been some attempts to construct accurate many-electron wavefunctions which start with the Hartree-Fock wave as the zero-order wavefunction.<sup>21</sup> For example, Kelly has applied the Brueckner-Goldstone approach to atoms, and Sinanoğlu has developed a variational treatment for finding a good perturbed wavefunction which apparently can be quite accurate and interpretable. We wish to point out that, although the Hartree-Fock wavefunction forms a rather good zero-order wavefunction for atoms and for molecules near the equilibrium configuration, it becomes an increasingly poor zero-order state as the internuclear distance increases. For example, the Hartree-Fock wavefunction for  $\text{H}_2$  has one doubly occupied orbital for all internuclear distances and dissociates to an energy 7.74 eV above the energy of the separated atoms, whereas there should be no correlation energy for separated hydrogen atoms. Thus, for large  $R$ , the perturbed wavefunction is very large if the Hartree-Fock wavefunction forms the zero-order state. One would like to have a zero-order state such that the perturbed wavefunction involves only true many-body effects—ones

<sup>21</sup> O. Sinanoğlu, Proc. Roy. Soc. (London) **A260**, 379 (1961); O. Sinanoğlu, J. Chem. Phys. **36**, 706, 3198 (1962); H. P. Kelly, Phys. Rev. **131**, 684 (1963); *ibid.* **144**, 39 (1966).

TABLE VI. Artifactual correlation energies for dissociated HF wavefunctions.

Molecule	Dissociation limit	Artifactual correlation energy	
		a.u.	eV
H <sub>2</sub> <sup>a</sup>	(H+H) + (H <sup>+</sup> +H <sup>-</sup> )	0.2846	7.744
LiH <sup>b</sup>	Li <sup>+</sup> +H <sup>-</sup>	0.2084	5.671
Li <sub>2</sub> <sup>c</sup>	(Li+Li) + (Li <sup>+</sup> +Li <sup>-</sup> )	0.1097	2.988
BH <sup>c</sup>	B <sup>+</sup> +H <sup>-</sup>	0.3035	8.258
CH <sub>4</sub> <sup>d</sup>	CH <sub>3</sub> <sup>+</sup> +H <sup>-</sup>	0.328	8.92

<sup>a</sup> Based on Hartree-Fock calculations for H<sub>2</sub> at  $R = \infty$  using optimized Slater orbitals with  $\zeta_{1s} = \zeta_{2s} = 1.455$  and  $\zeta_{1s}' = \zeta_{2s}' = 0.727$  on each center ( $E = -0.7154181$ ).

<sup>b</sup> Based on calculations by C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss [Rev. Mod. Phys. 32, 186 (1960)] and on a Hartree-Fock calculation on H<sup>-</sup> from a previous paper [W. A. Goddard, III, J. Chem. Phys. 48, 1008 (1968), Table I] ( $E = -0.4879297$ ).

<sup>c</sup> Based on Hartree-Fock calculations for Li<sub>2</sub> and for Li using the basis sets in Footnotes g and h of Table II, respectively.

<sup>d</sup> Based on Hartree-Fock wavefunctions for CH<sub>3</sub> ( $E = -39.46734$ ), CH<sub>3</sub><sup>+</sup> ( $E = -39.15179$ ), and CH<sub>3</sub><sup>-</sup> ( $E = -39.23124$ ), using the same basis set as in Table IV and on the Hartree-Fock wavefunction for H<sup>-</sup> mentioned in Footnote b.

<sup>e</sup> Based on calculations by E. Clementi, C. C. J. Roothaan, and M. Yoshimine [Phys. Rev. 127, 1618 (1962)] and references of footnote b.

which could not be treated by letting each electron move in an average field of the others—so that, for example, one could examine the changes in this true correlation as a function of interatomic distance (for a diatomic molecule) in order to ascertain its importance in binding. With such an ideal zero-order function the molecular correlation effects for the dissociated molecule would, of course, be zero, since the various atoms are infinitely far apart.

We wish to point out that the GF wavefunction possesses several important properties which would make it useful as a zero-order wavefunction in a perturbation treatment. Most important, the GF wavefunction dissociates properly and yet also provides a quite accurate description of the molecule near the equilibrium configuration (better than does the Hartree-Fock wavefunction). Since the GF wavefunction yields an independent particle interpretation, it can be said to not contain what should most reasonably be defined as correlation (viz., those interactions which necessarily involve the particles reacting to the instantaneous positions of the other particles). Hence, the perturbed wavefunction for this case would involve primarily only true correlation effects and could thus be expected to yield useful information concerning this complicated but perhaps important aspect of many-electron wavefunctions, especially in its relation to bonding. From Paper I the exact many-electron wavefunction can be written as

$$\psi_{\text{exact}}^{S,M} = \sum_{j_1 < j_2 < \dots < j_n, k_1 < \dots < k_m} C_{j,k} \times G_f(\phi_{j_1 a} \dots \phi_{j_n a} \phi_{k_1 b} \dots \phi_{k_m b} \chi_M), \quad (21)$$

where the  $a$  set of orbitals is complete and orthonormal,

as is the  $b$  set. This intraset orthogonality will be useful in the development of the perturbation scheme; however, even so, the appearance of two 1-electron Hamiltonians and nonorthogonality between  $a$  and  $b$  sets will lead to many complications which do not occur with schemes based on the Hartree-Fock method.

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## APPENDIX A

We will show that for a singlet state the GF wavefunction is left invariant under any permutation which takes all the  $a$  orbitals into  $b$  orbitals and vice versa. That is, if  $N=2n$  and  $S=0$  (thus the tableau is  $\gamma=[2^n]$ ), and if we let, say,

$$\tau_n = (1, n+1)(2, n+2) \dots (n, N),$$

then

$$G_f(\tau_n \Phi \chi) = G_f \Phi \chi.$$

The proof proceeds as follows: From Appendix E of Paper I,

$$U_{ff\tau_r} = 1 / \binom{n}{r},$$

where  $\tau_r$  is a product of  $r$  disjoint transpositions which take  $r$  indices  $\leq n$  to position  $> n$  and vice versa. Thus,

$$U_{ff\tau_n} = 1 / \binom{n}{n} = 1.$$

Of course this is only possible if  $n=m$ , since the maximum value of  $r$  is  $m$ . Using

$$G_f \tau_n \Phi \chi = \sum_r \zeta_{\sigma_r} (O_{rf} \tau_n \Phi) (\omega_{rf} \chi)$$

and

$$O^{\alpha}_{rf} \tau_n = \sum_{\beta p q} U^{\beta}_{p q \tau_n} O^{\alpha}_{rf} O^{\beta}_{p q} = \sum_q U^{\alpha}_{f q \tau_n} O^{\alpha}_{r q},$$

we note that  $U_{f q \tau_n} = 0$  if  $q \neq f$ , since  $U_{ff\tau_n} = 1$  and  $U$  is unitary. Hence,  $O^{\alpha}_{rf} \tau_n = O^{\alpha}_{rf}$ , and  $G_f \tau_n \Phi \chi = G_f \Phi \chi$ .

## APPENDIX B

Here we will derive a Koopmans' type theorem for GI orbitals. Consider  $\langle \Phi | H - E | O_{ii} \Phi \rangle = 0$ . Expanding this into terms which do not depend on  $\phi_k$ ,  $a_{N-1}$  and those which do, we obtain

$$0 = \langle \Phi | H - E | O_{ii} \Phi \rangle = a_{N-1} + \epsilon_{kk},$$

where (6) was used. In turn  $a_{N-1}$  may be expanded as  $A_{N-1} - EB_{N-1}$ , where  $B_{N-1}$  is the part of  $\langle \Phi | O_{ii} \Phi \rangle$  which does not involve  $\phi_k$ . Since  $B_{N-1}$  comes from those terms of  $O_{ii}$  which do not permute  $\phi_k$ , we have  $B_{N-1} = D_k^k$  (see Appendix B of III). Combining these equa-

tions, we have

$$E_N = (A_{N-1}/D_k^k) + (\epsilon_{kk}/D_k^k) = A'_{N-1} + e_k, \quad (\text{B1})$$

where (11) was used, and  $A'_{N-1} \equiv A_{N-1}/D_k^k$ .

Now consider the orbital corresponding to the last letter,  $N$ , of the tableau; in the GF case this is the orbital  $mb$ . If we denote the  $N$ -electron tableau by  $N$  and the one obtained by removing the  $N$ th letter by  $N-1$ , then

$$U_{ii\tau}^{N-1} = U_{ii\tau}^N$$

for all  $\tau$  which do not involve  $N$ . Thus, the  $A'_{N-1}$  from (B1) is equal to the energy of the  $N-1$  electron system (with tableau  $N-1$ ) obtained by deleting the  $N$ th orbital. That is,

$$E_N = E'_{N-1} + e_k. \quad (\text{B2})$$

However, (B2) is not restricted to just the  $N$ th orbital. If  $U_{ii\tau} = \pm 1$ , then  $\tau^{-1}O_{ii}\tau = O_{ii}$  (i.e.,  $O_{ii}\tau = \sum_{k,l} U_{kl\tau}^\beta O_{ii}^\beta O_{kl}^\beta = \sum_l U_{il\tau}^\alpha O_{ii}^\alpha = \pm O_{ii}^\alpha = \tau O_{ii}$ ). Thus, the energy

$$\begin{aligned} E &= \langle \Phi | HO_{ii} | \Phi \rangle / \langle \Phi | O_{ii} | \Phi \rangle \\ &= \langle \tau\Phi | HO_{ii} | \tau\Phi \rangle / \langle \tau\Phi | O_{ii} | \tau\Phi \rangle \end{aligned}$$

is invariant under permutation of the orbitals in  $\Phi$  by  $\tau$ . Hence, for all orbitals of  $\Phi$  which may be put in the  $N$ th position by some such  $\tau$ , we have (B2). For the GF case this includes all  $kb$  orbitals, and for singlet states all  $ka$  and  $kb$  orbitals (using the results of Appendix A). For the G1 case this includes all "nonpaired" orbitals for nonsinglet states (e.g., the  $2a$  orbital of Li) and all orbitals for singlet states. In addition, we have even seen in some other cases that (B2) is very nearly true. For example, in the GF wavefunction for Li,  $\langle \phi_{1a} | \phi_{1b} \rangle = 0.99989$  and  $A'_{N-1} = E_{N-1}$  within 0.00011 h out of  $-7.43281$  h.

From (B2) we see that if we approximate the state of the ionized molecule by removing the electron in the  $k$ th orbital and forcing the other  $N-1$  orbitals to remain unchanged, then  $-e_k$  is the ionization energy. There is still some possible arbitrariness here, however. For example, in the GF case it was shown in III that for any unitary transformation of the  $a$  orbitals among themselves and of the  $b$  orbitals among themselves, the many-electron wavefunction invariant. If

$$\{\phi_{1b}; i=1, \dots, m\}$$

are GF orbitals, consider

$$\psi_{jb} = \sum_{k=1}^m \phi_{kb} C_{kj} \quad j=1, \dots, m.$$

Then, since  $H^b\phi_{ib} = \epsilon_i^b\phi_{ib}$ , we have

$$H^b\psi_{jb} = \sum_{k=1}^m \epsilon_{kb} C_{kj} \phi_{kb} = \sum_{k=1}^m \psi_{kb} \eta_{kj},$$

where  $\eta_{kj} = \sum_i C_{ki}^{-1} \epsilon_{ib} C_{ij}$ . Since the  $\{\psi_{jb}\}$  are orthogonal, we again obtain Eq. (B2), this time with  $e_k$  replaced by  $\eta'_{kk} \equiv \eta_{kk}/D_k^k$ . Thus, one could have a continuum of values for the ionization energy. However, if  $E^{N-1} = E^N - \eta'_{kk}$  is required to be stationary under combinations of the  $\{\psi_{jb}\}$  orbitals among themselves, then the stationary values are just the  $e_{kb}$  (since these are the eigenvalues of the  $m$  by  $m$   $\langle \psi_{jb} | H^b | \psi_{kb} \rangle$  matrix). Thus, the  $-e_{kb}$  form nonarbitrary approximations to the ionization energies of the system. This is called Koopmans' theorem.<sup>6</sup>

In order to prevent confusion concerning what we mean by Koopmans' theorem, we should be more explicit. Koopmans considered the situation in which we have the unrestricted Hartree-Fock (UHF) wavefunction for an  $N$ -electron system (single Slater determinant and  $N$  spin orbitals,  $\{\psi_k\}$ ), and we wish to describe the  $N-1$  electron system by a single Slater determinant with  $N-1$  spin orbitals  $\{\psi'_k\}$ . Koopmans then made the restriction that *each  $\psi'_k$  be expanded in terms of the  $N$  occupied orbitals  $\{\psi_k\}$* . He showed that in this case the optimum choice of the  $\{\psi'_k\}$  is for each one to correspond to one of the  $\{\psi_k\}$  for the  $N$ -electron system. In addition he showed that in this approximation the ionization energy is given by minus the orbital energy for the spin orbital removed. In the GF case we do the analogous thing. We start with the GF wavefunction for an  $N$ -electron system with spin  $S = \frac{1}{2}(n-m)$  and orbitals  $\{\phi_{ia}\}$  and  $\{\phi_{ib}\}$ . For the  $N-1$  electron system we also use a  $G_r\chi$ -type wavefunction, but with orbitals  $\{\phi'_{ia}\}$  and  $\{\phi'_{ib}\}$  in the product  $\Phi$ . Then, we take each  $\phi'_{ia}$  to be expanded in terms of the occupied  $\{\phi_{ia}\}$  and each  $\phi'_{ib}$  to be expanded in terms of the occupied  $\{\phi_{ib}\}$ . If we do this, we find that the optimum occupied  $\{\phi'_{ia}\}$  and  $\{\phi'_{ib}\}$  just correspond to the GF orbitals for the  $N$ -electron system. In addition, the ionization energy is again given by minus the orbital energy. In either case (UHF or GF), the predicted ionization energy is close to the experimental value only if the additional error in describing the  $N-1$  electron system balances the difference in correlation energies for the  $N-1$  and  $N$ -electron systems.